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# Direct Reaction Between Copper and Nitrogen at High Pressures and Temperatures

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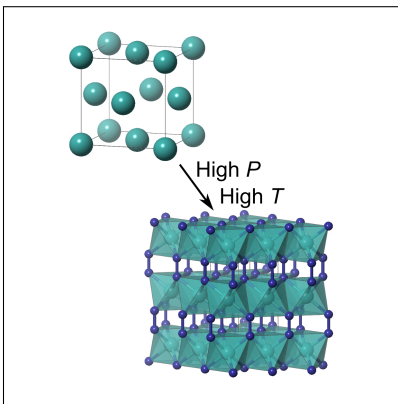
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## Abstract

Transition metal nitrides have applications in a range of technological fields. Recent experiments have shown that new nitrogen-bearing compounds can be accessed through a combination of high temperatures and pressures, revealing a richer chemistry than was previously assumed. Here, we show that at pressures above 50 GPa and temperatures greater than 1500 K the elemental copper reacts with nitrogen forming copper diazenide ( $\text{CuN}_2$ ). Through a combination of synchrotron X-ray diffraction and first-principles calculations we have explored the stability and electronic structure of  $\text{CuN}_2$ . We find that the novel compound remains stable down to 25 GPa before decomposing to its constituent elements. Electronic structure calculations show that  $\text{CuN}_2$  is metallic and exhibits partially filled  $\text{N}_2$  antibonding orbitals, leading to an ambiguous electronic structure between  $\text{Cu}^+/\text{Cu}^{2+}$ . This leads to weak Cu-N bonds and the lowest bulk modulus observed for any transition metal nitride.

## Graphical TOC Entry



Nitrogen is largely inert under atmospheric conditions however, it forms a large number of technologically important materials with main group elements and transition metals. Nitride compounds have been an important focus of inorganic chemistry for many decades, typically synthesised at high temperatures.<sup>1</sup> Recently, alternative high-pressure synthesis methods have provided highly successful for the discovery of novel materials which have been proposed as ideal candidates in a range of areas from highly non-compressible materials<sup>2-4</sup> to explosives.<sup>5,6</sup>

Solids with polymeric networks of N-N single bonds<sup>7,8</sup> should act as excellent high energy density materials if suitable synthesis routes can be found. Extensive theoretical work has predicted the existence of poly-nitride species for at least sixteen metals (*e.g.* Refs<sup>9-14</sup>) and recent experiments have begun to test these predictions, uncovering intriguing structures containing polymeric nitrogen chains,<sup>15</sup> molecular inclusion compounds,<sup>16</sup> and pentazolate anions,<sup>17,18</sup> all synthesised under high-pressure and high-temperature reaction conditions.

The platinum-group metals (Pt,<sup>2</sup> Pd,<sup>4</sup> Rh,<sup>19</sup> Os<sup>3</sup> Ir,<sup>3,20</sup> and Ru<sup>21</sup>) have been shown to form highly incompressible N-containing species. Although they crystallise in a range of different structures, these compounds share a number of features leading to high bulk moduli primarily N-N single bonds ( $\approx 1.4$  Å) linking octahedrally coordinated N atoms.<sup>22</sup> Numerous subsequent experimental and theoretical studies have continued to search for ultrahard materials amongst other transition-metal nitrides at high pressure.<sup>9,11,23-25</sup>

The coinage metals (group 11: Cu, Ag, and Au) have so far shown a limited propensity to form nitrogen-bearing compounds despite intense efforts utilising an array of synthesis techniques including nitrogen-ion irradiation.<sup>26-29</sup> Copper is known to form two nitrogen-containing compounds; copper azide ( $\text{CuN}_3$ ), a highly sensitive explosive,<sup>30</sup> and copper nitride ( $\text{Cu}_3\text{N}$ ) a stable semiconductor finding applications in a wide range of areas from lithium-ion battery electrodes to conductive ink and solar energy harvesting.<sup>31-33</sup> Under compression, the narrow band gap (0.6 eV) of  $\text{Cu}_3\text{N}$  closes by  $\approx 5$  GPa and no structural phase transitions are observed up to 26.7 GPa.<sup>34</sup> Silver also forms an explosive azide ( $\text{AgN}_3$ )<sup>35</sup>

and attempts at forming stable gold nitrides have been limited to ion-irradiated surfaces.<sup>26,28</sup>

Here, using a combination of high-pressure and high temperatures, we have explored the synthesis of novel copper-nitrogen compounds. After laser heating at 50 GPa, we observe the direct reaction between copper and nitrogen forming a previously unknown copper diazenide with stoichiometry  $\text{CuN}_2$ . This compound is stable on decompression down to 25 GPa before decomposing to its constituent elements. Calculations show  $\text{CuN}_2$  is a metal with a copper oxidation state lying between +1 and +2. As a result  $\text{CuN}_2$  contains highly compressible Cu-N bonds giving mechanical properties far more in common with alkaline earth diazenides<sup>36–38</sup> than other transition metal nitrides.

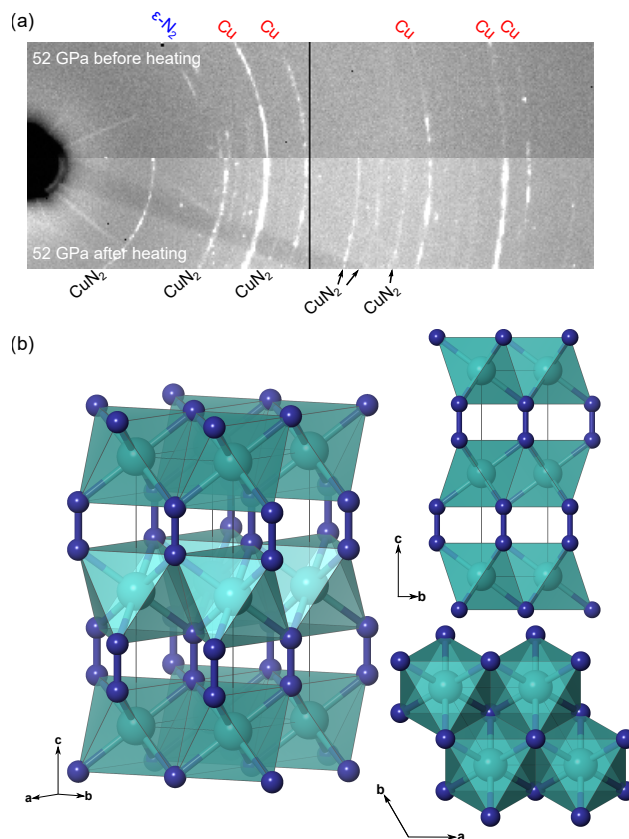


Figure 1: High pressure X-ray diffraction patterns ( $\lambda = 0.3344 \text{ \AA}$ ) showing (a) the synthesis of  $\text{CuN}_2$  by laser heating at 52 GPa; (b) Crystal structure of  $\text{CuN}_2$ , Cu atoms are green, N atoms blue. Optimised structural parameters derived from DFT calculations at 52 GPa:  $a = 2.741$ ,  $c = 7.0417 \text{ \AA}$ ,  $\text{Cu}[2a (0, 0, 0)]$ ,  $\text{N}[4f (\frac{1}{3}, \frac{2}{3}, 0.6650)]$ .

Samples of Cu powder were compressed in solid  $\text{N}_2$  and laser heated at 10 GPa intervals

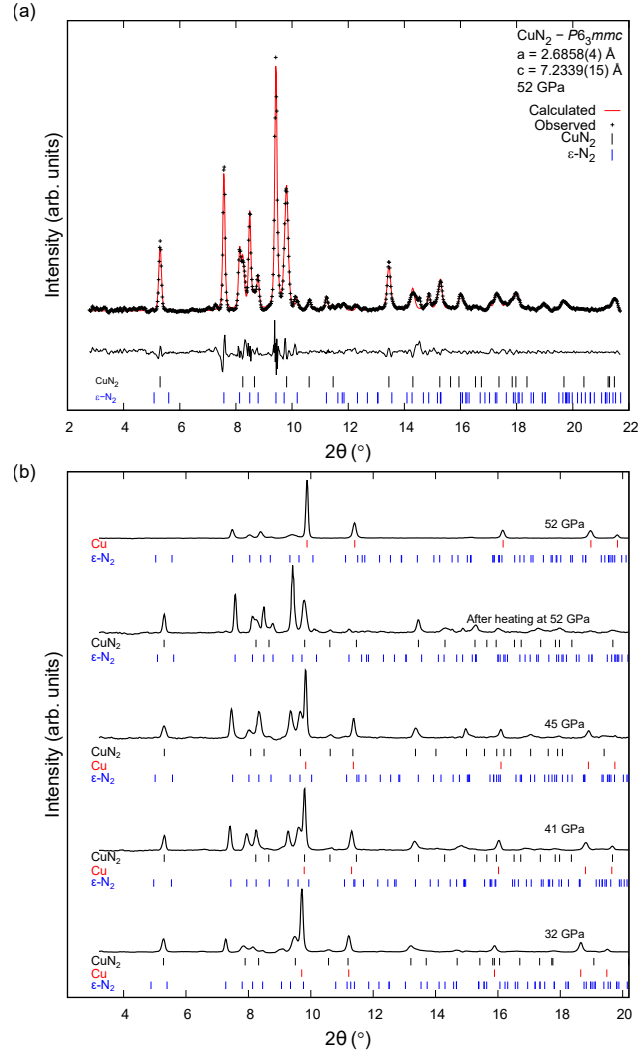


Figure 2: Representative Le Bail refinement of  $\text{CuN}_2$  data at 52 GPa  $wR_p = 0.39$  ( $\lambda = 0.3344 \text{ \AA}$ ); (b) Synthesis and decompression of  $\text{CuN}_2$ , tick marks indicated Bragg reflection positions for the noted phase.

up to 50 GPa with no observed changes in diffraction patterns with the exception of the known phase transitions in pure N<sub>2</sub>.<sup>39,40</sup> Above 52 GPa the Cu sample coupled strongly, with temperatures in excess of  $\sim 1500$  K. Upon quenching numerous new diffraction lines appeared (Figure 1(a)), all of which could be indexed to a hexagonal unit cell [ $a = 2.6759(5)$ ,  $c = 7.235(3)$  Å, at 52 GPa], with systematic absences indicating the presence of a  $c$ -glide normal to  $[1\bar{1}1]$ . Attempts to solve the crystal structure were hindered by numerous overlapping reflections from  $\epsilon$ -N<sub>2</sub>, however a possible solution was found by direct methods in space group  $P6_3/mmc$ ,<sup>41</sup> with stoichiometry CuN<sub>2</sub>. Rietveld refinement required excluding regions of the profile which overlapped with peaks due to  $\epsilon$ -N<sub>2</sub> as diffraction from  $\epsilon$ -N<sub>2</sub> took the form of quasi-single crystal diffraction peaks unsuitable for inclusion in the refinement. Due to the poor quality of the data the nitrogen-atom position was poorly defined giving a large uncertainty on the experimentally determined N-N bond distance (1.3(3) Å). However, despite extensive overlapping, unit-cell dimensions of this new phase could be extracted (Figure 2(b)) and the resulting changes in unit-cell volume with pressure (Figure 3(a)) also suggest a stoichiometry of CuN<sub>2</sub>. To confirm our experimental structural analysis and to explore the electronic structure of CuN<sub>2</sub> we have performed DFT geometry optimisation calculations. We find that the structure converges to close agreement with experimentally determined unit-cell dimensions (Figure 3(b)).

The optimised structure of the novel compound CuN<sub>2</sub> contains octahedrally coordinated Cu atoms, in common with many transition metal-nitrogen compounds (e.g. PtN<sub>2</sub><sup>2</sup> and FeN<sub>2</sub><sup>15</sup>). These edge-sharing CuN<sub>6</sub> octahedra are arranged in layers in the  $ab$ -plane and are linked by N<sub>2</sub> anions aligned along the  $c$ -axis, with a N-N interatomic distance of 1.197 Å at 52 GPa. (Figure 1(b)). This N-N distance gives a direct insight into the nature of the electronic structure of transition metal nitrides. In cases with high metal oxidation states, the transfer of electron density from the metal results in “pernitride” anions ( $[\text{N-N}]^{4-}$ ) which form strong  $M$ -N bonds, have high bulk moduli, and show internal N-N distances of approximately 1.4 Å, seen in the archetypal examples of PtN<sub>2</sub>,<sup>2</sup> OsN<sub>2</sub><sup>3</sup> and TiN<sub>2</sub>.<sup>24</sup> If the metal is limited to an

oxidation state of +2, “diazenide” ( $[\text{N}=\text{N}]^{2-}$ ) anions are formed instead. In these compounds  $M$ -N bonding is weaker, bulk moduli are lower, and the internal N-N distances are shorter,  $\approx 1.2$  Å. This is the case for the alkaline earth metal diazenides,  $\text{BaN}_2$  and  $\text{SrN}_2$ .<sup>42</sup> The short N-N distance in  $\text{CuN}_2$  (1.197 Å) would appear to suggest that, by analogy, in this compound Cu is present as  $\text{Cu}^{2+}$  and is bonded to  $[\text{N}=\text{N}]^{2-}$  anions. However, a  $\text{Cu}^{2+}$  ion would be expected to display a Jahn-Teller distortion which is not consistent with proposed crystal structure. To understand this discrepancy, lattice dynamics calculations were carried out at 0 and 50 GPa, and at both pressures the  $P6_3/mmc$  structure is dynamically stable and all phonons are real, indicating the absence of a driving force to distort the  $\text{CuN}_6$  octahedra. Furthermore, geometry optimisation of a distorted structure in the orthorhombic subgroup  $Cmcm$  resulted in a return to  $P6_3/mmc$  symmetry within numerical accuracy.

A more detailed understanding of the electronic structure of  $\text{CuN}_2$  is gained through the crystal orbital Hamiltonian population (COHP) analysis.<sup>43,44</sup> The electronic density of states of  $\text{CuN}_2$  is shown in Figure 4(a). This shows  $\text{CuN}_2$  to be a metal with no clear character to the states at the Fermi level, but it is dominated by Cu-3*d* and N-2*p* states as expected. There is a gap at 4 eV above the Fermi level corresponding to additional unfilled  $\text{N}_2$   $1\pi_g^*$  and  $2\sigma_u^*$  states. A more quantitative picture arises from the integration of the COHP(N-N) over the energy range of these antibonding orbitals from  $-5$  to  $5$  eV as seen in (Figure 4(b)). The resulting 32.5% occupancy is significantly less than the 50% expected for  $[\text{N}=\text{N}]^{2-}$  anions<sup>38</sup> and, combined with the absence of a Jahn-Teller distortion, intriguingly supports an ambivalent electronic state between  $[\text{N}=\text{N}]^-$  and  $[\text{N}=\text{N}]^{2-}$ .

From the synthesis pressure, samples were decompressed to determine the stability of this newly synthesised copper diazenide. Below 25 GPa peaks due to  $\text{CuN}_2$  disappear leaving only those from Cu and  $\epsilon\text{-N}_2$ . Changes in unit-cell volume with pressure were fitted with a Vinet equation of state giving a bulk modulus of  $K_0(\text{CuN}_2) = 130(11)$  GPa, extremely close to that of Cu (140 GPa) and comparable to the low bulk moduli observed for the alkaline earth metal diazenides [ $K_0(\text{BaN}_2) = 46$  GPa,  $K_0(\text{SrN}_2) = 65$  GPa].<sup>42</sup> Unsurprisingly then,



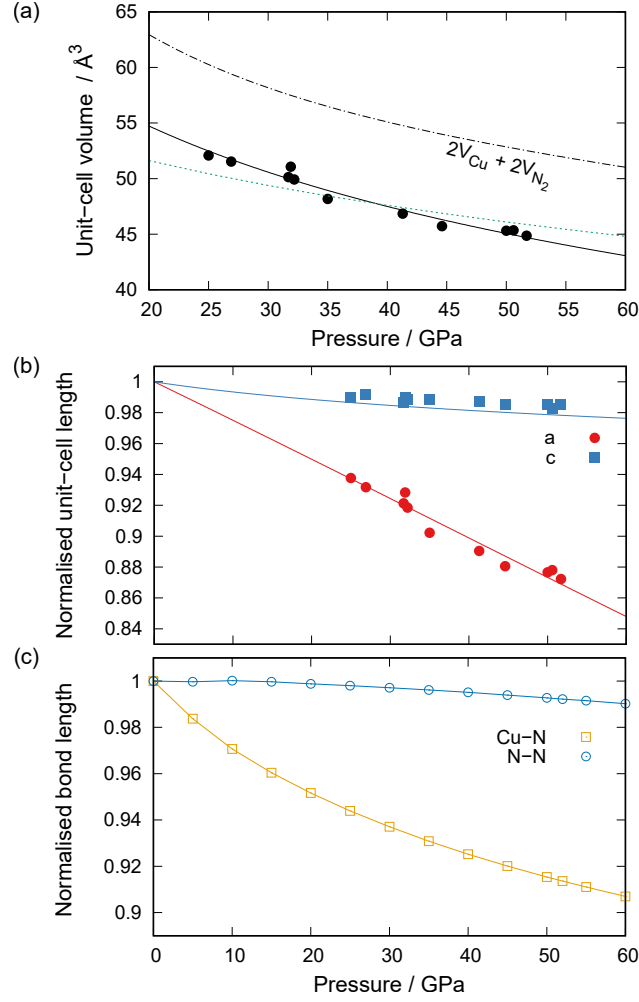


Figure 3: (a) Change in CuN<sub>2</sub> unit-cell volume with pressure, dashed line indicates volume of pure Cu + N<sub>2</sub> for comparison. Solid line indicates fitted Vinet equation of state ( $V_0 = 62.3(13) \text{ \AA}^3$ ,  $K_0 = 130(11) \text{ GPa}$ ,  $K' = 1$ ), dotted line shows the unit-cell volume derived from DFT calculations; (b) Changes in normalised unit-cell lengths for CuN<sub>2</sub>,  $a_0$  and  $c_0$  derived from calculations; (c) Changes in normalised bond lengths for Cu-N (yellow squares) and N-N (blue circles) with pressure.

the overall compressibility appears very similar to that calculated from the pure elements (Figure 3(a)).

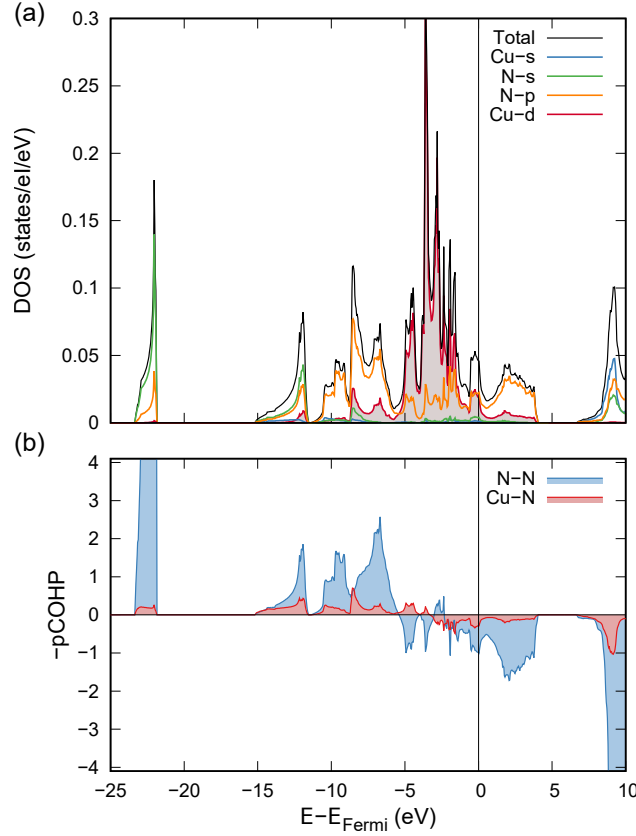


Figure 4: (a) Electronic density of states, (b) COHP analysis of  $\text{CuN}_2$  at 50 GPa.

Closer analysis shows the majority of this compression is taken up by the  $a$  and  $b$  axes, by 52 GPa the  $a$  axis decreases by 12.8 % ( $-0.392(5)$  Å) relative to the calculated ambient pressure value as compared to the far more rigid  $c$  axis which decreases by just 0.65 % ( $-0.047(3)$  Å) over the same pressure range (Figure 3(b)). The origin of this anisotropic behaviour lies in the contrasting strengths of Cu-N and N-N bonding, as shown in Figure 3(c). As would be expected for a strongly-bonded diazenide anion, N=N distance reduces by less than 1% up to 60 GPa, almost an order of magnitude more resilient than the Cu-N bonds which compress by  $-9.3\%$ . The presence of highly compressible  $M$ -N bond and the resulting low bulk modulus again marks  $\text{CuN}_2$  as being far more similar to the alkaline earth diazenides rather than other transition metal nitrides. This is the logical conclusion to the

trend observed across the first-row transition metal nitrides  $MN_2$ , as the  $N_2$  anion shows greater molecular character,  $M$ -N bonds weaken and bulk moduli reduce:  $K_0(\text{TiN}_2) = 382(3)$  GPa,<sup>24</sup>  $K_0(\text{FeN}_2) = 344(13)$  GPa,<sup>25</sup>  $K_0(\text{CoN}_2) = 216(18)$  GPa<sup>45</sup> and  $K_0(\text{CuN}_2) = 130(11)$  GPa.

In conclusion, we have utilised *in situ* laser heating combined with high pressures to perform the first direct reaction between elemental nitrogen and a coinage metal to form a novel copper diazenide ( $\text{CuN}_2$ ) compound. The structure was determined by a combination of powder X-ray diffraction and DFT calculations. Surprisingly for a transition metal nitride,  $\text{CuN}_2$  is highly compressible due to the presence of extremely weak Cu-N bonds. The origins of this surprising behaviour lie in the limited electron transfer between Cu and  $N_2$ . Electronic structure analysis indicates partially-filled antibonding orbitals on the  $N_2$  anions which combined with the absence of a Jahn-Teller distortion, suggests an electronic structure between  $\text{Cu}^+[\text{N}=\text{N}]^-$  and  $\text{Cu}^{2+}[\text{N}=\text{N}]^{2-}$ . This compound remains stable down to 25 GPa before decomposing to its constituent elements.

High purity copper powder (99.8%, 1.6  $\mu\text{m}$  particle size) from Alfa Aesar was placed into diamond-anvil cells (DAC) and subsequently loaded with high purity nitrogen gas (99.9%) at 0.17 GPa. Loading of nitrogen was confirmed by the observation of the nitrogen vibrational mode using a custom-built micro-focused Raman system.<sup>46</sup> Rhenium gaskets were used to form the sample chamber in all experimental runs with diamond-anvil culets ranging from 200 to 300  $\mu\text{m}$ .

The Cu-sample was heated *in-situ* from both sides uniaxially by directly coupling to an yttrium-aluminium-garnet (YAG) laser with wave-length  $\lambda = 1064$  nm. Angle-dispersive X-ray diffraction data were collected at beamline 13-IDD (GSECARS) at APS, USA.<sup>47</sup> The diffraction from 0.3344 Å wavelength X-rays was recorded using a Pilatus 1M image-plate detector. Two-dimensional image-plate data were integrated with *DIOPTAS* to yield intensity *vs.*  $2\theta$  plots.<sup>48</sup> Diffraction patterns were indexed with *CONOGRAPH*,<sup>49</sup> Le Bail and Rietveld refinement was carried out in *Jana2006*.<sup>50–52</sup>

Total energy calculations were carried out within the framework of density functional theory (DFT) in conjunction with the projector-augmented wave method and a plane wave basis, as implemented in the VASP code.<sup>53,54</sup> We used the PBE exchange-correlation functional<sup>55</sup> and included the Cu  $3p$ ,  $4s$ , and  $3d$  and N  $2s$  and  $2p$  electrons in the valence space. Brillouin zone sampling was done on regular  $k$ -point grids with linear densities of  $50 / \text{\AA}^{-1}$ , the plane wave cutoff energy was 1000 eV. Structures were optimised over a sequence of pressures until remaining forces on the atoms were smaller than 1 meV/ $\text{\AA}$ . Partial DOS and COHP analysis carried out using LOBSTER.<sup>56</sup>

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